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# Anomalous heavy atom effect on optical limiting property of homoleptic double-decked sandwich-type lanthanide diphthalocyanines

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## Abstract

Optical limiting (OL) performance of two homoleptic sandwich-type lanthanide diphthalocyanines,  $M[\text{Pc}(\text{OC}_5\text{H}_{11})_8]_2$  ( $M = \text{Gd}, \text{Eu}$ ), was investigated via fluence-dependent transmittance measurements. The measurements were performed using collimated 10-ns pulses generated from a frequency-doubled Nd:YAG laser at 532-nm wavelength. The results indicated that  $\text{Eu}[\text{Pc}(\text{OC}_5\text{H}_{11})_8]_2$  exhibited better OL performance than  $\text{Gd}[\text{Pc}(\text{OC}_5\text{H}_{11})_8]_2$ , which seems to be contrary to the heavy atom effect because the gadolinium ion is heavier than europium ion. A possible explanation was proposed that, not only the atomic number but also the ion radius of the metal center would influence the OL performance of metal diphthalocyanines. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The development of optical limiting (OL) materials has attracted considerable attention [1–5] to satisfy the increasing need for protecting human eyes and optical sensors from exposure to undesired intense laser beams. Among several nonlinear optical mechanisms for OL, reverse saturable absorption (RSA) [3,5] is considered to be the most

important one, in which the OL for nanosecond laser pulses resulted from the strong triplet–triplet absorption and large absorption cross-section ratio of triplet state to ground state. High inter-system crossing yield from the singlet state to the triplet state and long triplet state lifetime are favorable for the accumulation of triplet-state population, so they are in favor of the OL for nanosecond laser pulses that originated from RSA.

Phthalocyanines (Pcs) have been shown [6–9] to be excellent OL materials that based on RSA for nanosecond 532-nm laser pulses because of their relatively low linear absorption and high absorption cross-section ratio of excited state to ground

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state in the range of 400–600 nm. Moreover, metal phthalocyanines (MPcs) played even better [2,7] than metal-free Pcs and this was due to the heavy atom effect. This effect can facilitate intersystem crossing from singlet state to triplet state via spin-orbital coupling and thus reinforce the absorption of triplet state by increased population. However, to the extent of our knowledge, MPcs which have been demonstrated to have heavy atom effect in OL behavior are all two-dimensional and with symmetry  $D_{4h}$  because of the small radius of the encompassed metal ions.

Sandwich-type metal diphthalocyanines, in which the large conjugated  $\pi$  systems are held in close proximity by metal ions of larger radius such as rare earth metals and transitional metals, have also been synthesized and found widespread applications in materials science, especially in electrochromism [10,11], intrinsic molecular conductivity [12] and gas-sensing property [13]. The UV–VIS spectra of diphthalocyanines were displayed [14,15] to be rather complex than that of planar Pc monomers [7] because the intramolecular  $\pi$ – $\pi$  interaction between the two Pc macrocycles might lead to a splitting of the degenerate molecular orbitals of each monomer. We have investigated the OL performance of two sandwich-type lanthanide diphthalocyanines  $\text{Eu}[\text{Pc}(\text{R})_8]_2$  ( $\text{R} = n\text{-C}_7\text{H}_{15}, \text{OC}_5\text{H}_{11}$ ) and compared the effect of different peripheral ligands on it [16]. To make clear whether the heavy atom effect on OL performance still hold true in metal diphthalocyanines, in this letter, the OL behavior of two sandwich-type lanthanide diphthalocyanines,  $\text{M}[\text{Pc}(\text{OC}_5\text{H}_{11})_8]_2$  ( $\text{M} = \text{Gd}, \text{Eu}$ ), was studied and compared under the same condition.

## 2. Experiment

The synthesis process of the two lanthanide diphthalocyanines,  $\text{M}[\text{Pc}(\text{OC}_5\text{H}_{11})_8]_2$  ( $\text{M} = \text{Gd}, \text{Eu}$ ), is referred to Ref. [17]. Their schematic diagrams are displayed in Fig. 1. The trivalent ions are sandwiched by two parallel but staggered Pc macrocycles. Because of the strong intermolecular  $\pi$ – $\pi$  interaction, MPc molecules in solution have the propensity to aggregate, especially at a high

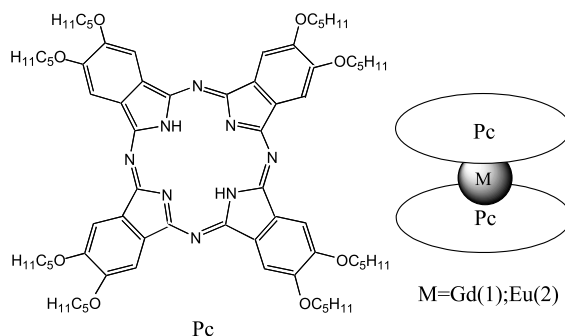


Fig. 1. Schematic diagram of molecular structures of  $\text{Gd}[\text{Pc}(\text{OC}_5\text{H}_{11})_8]_2$  (1) and  $\text{Eu}[\text{Pc}(\text{OC}_5\text{H}_{11})_8]_2$  (2).

concentration [18] or the solvent having high polarity [19]. In order to suppress the aggregation, the two MPcs were dissolved in chloroform with low concentrations. Both of them were finally prepared in 5 mm thickness glass cells with two linear transmittances, 72% and 65%.

Experiments for fluence-dependent transmittance measurements were performed using 532-nm wavelength, 10-ns laser pulses from a frequency-doubled Quantel Q-switched Nd:YAG laser. The experimental setup was similar to that used in our previous work [20,21] as shown in Fig. 2. The laser output was spatially filtered by a diaphragm and a nearly homogeneous light spot was obtained. Then, the laser beam was collimated to a smaller size by an inverted telescope system, which was conformed by a convex lens ( $f = 15$  cm) and a concave lens ( $f = -5$  cm). Before entering the sample, the collimated laser beam was separated to two parts by a beam splitter, BS. The weak part was detected with an Rjp-735 energy probe (Laser Precision Corporation, USA) in order to monitor the incident laser energy. The strong one was transmitted onto the glass cell, which was filled

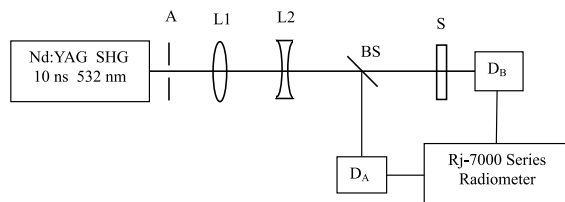


Fig. 2. Experimental setup used for fluence-dependent transmittance measurements.

with the sample solution. The light spot on the sample was measured to be of 1.3 mm diameter by razor method. The transmitted pulse energy was detected with another energy probe (Rjp-734, Laser Precision Corporation, USA). Compared with the light spot dimension, the much larger acceptance area of the energy probes ensured that a collection of all the energy of the pulse and thus the factor of nonlinear refraction was excluded. To avoid the influence of thermal effect, a single pulse measurement was used so that each pulse of light was certain to encounter fresh molecules in the sample.

### 3. Results and discussion

The experimental results of output–input characteristics are shown in Figs. 3 and 4 for linear transmittances of 72% and 65% respectively. No matter under which concentration, the transmittances of the two solutions both decrease remarkably with the increased laser intensity and the OL performance of  $\text{Eu}[\text{Pc}(\text{OC}_5\text{H}_{11})_8]_2$  is slightly better than that of  $\text{Gd}[\text{Pc}(\text{OC}_5\text{H}_{11})_8]_2$ .

A phenomenological model for nonlinear absorption proposed by Golovlev [22] was adapted to fit our experimental results. In this model, the absorption cross-section  $\sigma$  is expressed in the form of a series expansion of the laser fluence  $\Phi$ :

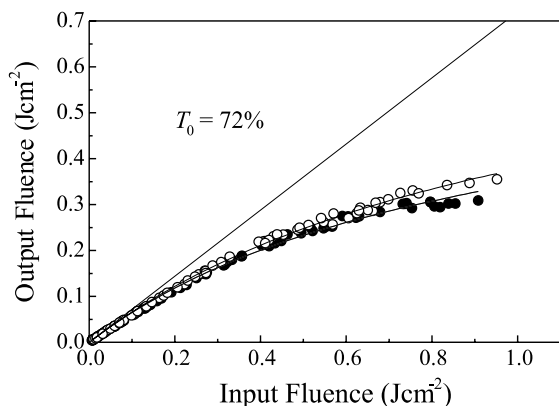


Fig. 3. Output–input characteristics of  $\text{Gd}[\text{Pc}(\text{OC}_5\text{H}_{11})_8]_2$  (○) and  $\text{Eu}[\text{Pc}(\text{OC}_5\text{H}_{11})_8]_2$  (●) in chloroform solutions of 72% linear transmittance at 532 nm.

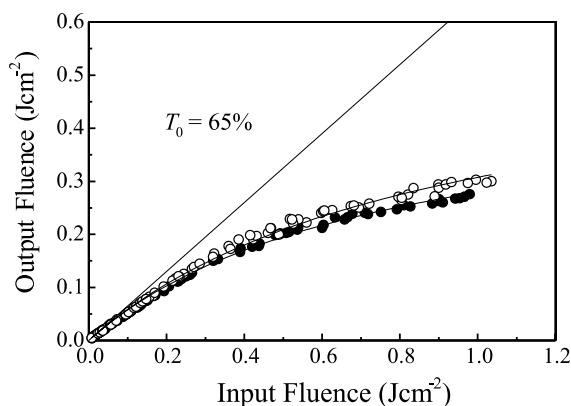


Fig. 4. Output–input characteristics of  $\text{Gd}[\text{Pc}(\text{OC}_5\text{H}_{11})_8]_2$  (○) and  $\text{Eu}[\text{Pc}(\text{OC}_5\text{H}_{11})_8]_2$  (●) in chloroform solutions of 65% linear transmittance at 532 nm.

$$\sigma(\Phi) = \sigma_0 + \mu_1\Phi + \mu_2\Phi^2 + \dots \quad (1)$$

Retaining the first two terms of this expansion and putting Eq. (1) into the Beer's law, the laser fluence propagating equation in the medium can be obtained, and then by integrating the expression of output laser fluence can be easily got:

$$\Phi_{\text{out}} = T_0\Phi_{\text{inp}}/[1 + (1 - T_0)\Phi_{\text{inp}}/\Phi_{\text{nl}}] \quad (2)$$

where  $T_0 = \exp(-\sigma_0 N_0 L)$  is the linear transmittance;  $\Phi_{\text{inp}}$  and  $\Phi_{\text{out}}$  are the input and output laser fluence respectively; and  $\Phi_{\text{nl}} = \sigma_0/\mu_1$ . It can be seen from Eq. (2) that in this model the OL performance of a sample can conveniently be assessed by only the value of  $\Phi_{\text{nl}}$ . The smaller magnitude of  $\Phi_{\text{nl}}$  denotes the better OL performance of the sample.

The experimental results were fitted with Eq. (2) and the best fitting results are shown in Figs. 3 and 4 with solid curves. Under the two concentrations, the values of  $\Phi_{\text{nl}}$  of  $\text{Eu}[\text{Pc}(\text{OC}_5\text{H}_{11})_8]_2$  and  $\text{Gd}[\text{Pc}(\text{OC}_5\text{H}_{11})_8]_2$  got from the best fitting results are both 0.26 and 0.31  $\text{J cm}^{-2}$  respectively. The latter is 1.2 times the former. This congruency indicates that the OL performance of  $\text{Gd}[\text{Pc}(\text{OC}_5\text{H}_{11})_8]_2$  is 1.2 times worse relative to that of  $\text{Eu}[\text{Pc}(\text{OC}_5\text{H}_{11})_8]_2$ . This result seems to be contrary to the heavy atom effect on OL because the gadolinium ion is heavier than europium ion.

UV–VIS spectra of both lanthanide dipt-halocyanines,  $\text{M}[\text{Pc}(\text{OC}_5\text{H}_{11})_8]_2$  ( $\text{M} = \text{Gd}, \text{Eu}$ ), are

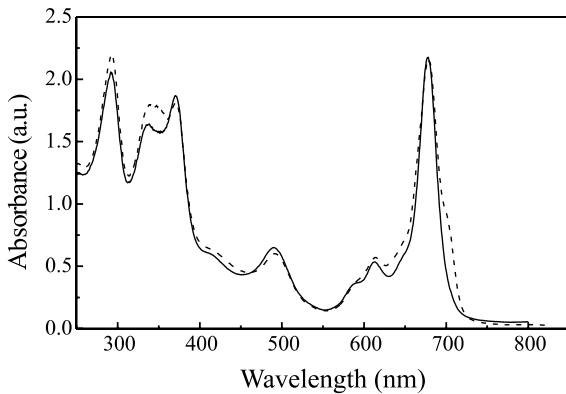


Fig. 5. UV-VIS spectra of  $\text{Gd}[\text{Pc}(\text{OC}_5\text{H}_{11})_8]_2$  (—) and  $\text{Eu}[\text{Pc}(\text{OC}_5\text{H}_{11})_8]_2$  (- - -) both in chloroform.

shown in Fig. 5. The absorption of  $\text{Gd}[\text{Pc}(\text{OC}_5\text{H}_{11})_8]_2$  exhibits slightly larger splitting between the two peaks in Q band and stronger shoulder at 590 nm relative to that of  $\text{Eu}[\text{Pc}(\text{OC}_5\text{H}_{11})_8]_2$ . From this, the stronger  $\pi$ - $\pi$  interaction between the two Pc rings of  $\text{Gd}[\text{Pc}(\text{OC}_5\text{H}_{11})_8]_2$  than that of  $\text{Eu}[\text{Pc}(\text{OC}_5\text{H}_{11})_8]_2$  could be concluded [23]. It is consistent with the smaller radius of the gadolinium ion relative to that of europium ion because the small size of the metal center would result in the small ring-to-ring separation and then the strong intramolecular  $\pi$ - $\pi$  interaction between the two Pc rings in the metal diphthalocyanines [23,24]. The strong  $\pi$ - $\pi$  interaction usually adds relaxation pathway and thus results in shortened triplet-state lifetime [9,25], which is adverse to the triplet-state absorption by reducing the triplet-state population accumulation. So, the small metal ion radius would go against the OL performance of metal diphthalocyanines for nanosecond laser pulses that based on RSA. Hence, the OL performance of metal diphthalocyanines for nanosecond laser pulses depends not only on the metal atomic number but also on the metal ion radius. It is the synthetic effect of the counteractive of small radius and the reinforcing function of the large atomic number.

In these two investigated diphthalocyanines,  $\text{M}[\text{Pc}(\text{OC}_5\text{H}_{11})_8]_2$  ( $\text{M} = \text{Gd}, \text{Eu}$ ), the better OL behavior of  $\text{Eu}[\text{Pc}(\text{OC}_5\text{H}_{11})_8]_2$  than that of  $\text{Gd}[\text{Pc}(\text{OC}_5\text{H}_{11})_8]_2$  demonstrated that the coun-

teractive of smaller gadolinium ion radius is stronger than the reinforcing function of the larger gadolinium atomic number.

#### 4. Conclusion

In summary, OL performance for 532-nm 10-ns laser pulses of sandwich-type lanthanide diphthalocyanines,  $\text{M}[\text{Pc}(\text{OC}_5\text{H}_{11})_8]_2$  ( $\text{M} = \text{Gd}, \text{Eu}$ ), was investigated under identical conditions. Through comparison  $\text{Eu}[\text{Pc}(\text{OC}_5\text{H}_{11})_8]_2$  exhibited a superiority than  $\text{Gd}[\text{Pc}(\text{OC}_5\text{H}_{11})_8]_2$  for OL. This was attributed to the smaller ion radius of gadolinium than that of europium, because it shortens the ring-to-ring separation and then strengthens the intramolecular  $\pi$ - $\pi$  interaction of  $\text{Gd}[\text{Pc}(\text{OC}_5\text{H}_{11})_8]_2$ . A conclusion that the OL performance of metal diphthalocyanines for nanosecond laser pulses is the synthetic effect of the counteractive of small size and the reinforcement function of the large atomic number was arrived.

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